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(54) **A fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region**

(57) A fluorophosphate fluorescent glass of the present invention, capable of converting invisible ultraviolet rays into visually observable visible rays with high efficiency and available for controlling the optical axis of a laser beam such as an excimer laser has a chemical composition comprising, at least, (I) phosphorus (P), oxygen (0) and fluorine (F), as glass constituting components, and (II) at least one member selected from divalent europium, terbium and (samarium + manganese), as a fluorescent agent, the divalent europium being contained as an essential component and at least one of samarium and manganese being contained as an essential component when terbium is present. In particular, a fluorophosphate fluorescent glass exhibiting a blue fluorescence containing europium as an essential component and a fluorophosphate fluorescent glass exhibiting a white fluorescence containing at least one of samarium and manganese as an essential component are provided.

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Description

This invention relates to a fluorophosphate fluorescent glass exhibiting a visible fluorescence and, more particularly, it is concerned with a fluorophosphate fluorescent glass exhibiting a blue fluorescence, which is capable of converting invisible ultraviolet rays into visually observable visible-rays with high efficiency and is available for controlling the optical axis of a laser beam such as an excimer laser, and applicable to fluorescent displaying of full color in combination with a green or red fluorescent glass, or a fluorophosphate fluorescent glass exhibiting white fluorescence, which can be utilized for display devices and backlights of LCDs.

Phosphors using rare earth elements have widely been used up to the present time, mainly as phosphors, for example, for lamps and color picture tubes. Of late, materials for the anti-Stokes-wise wavelength conversion of infrared light into visible light have extensively been studied, for example, for application to laser materials.

The trivalent Eu ion showing a fluorescence with a narrow spectrum width in the red region has been put into practice for color pictures tubes and high color rendering fluorescent lamps. The divalent Eu ion obtained by reducing the trivalent Eu ion, capable of exhibiting various fluorescences depending on materials, has been put to practical use as in materials for X-ray intensifying screens, and high color rendering fluorescent lamps.

Tb ion exhibiting green fluorescence and Mn ion exhibiting red fluorescence have been put to practical use in materials for color picture tubes, and high color rendering fluorescent lamps. As described above, phosphors using Tb, Eu and Mn have already been put to practical use, but such a phosphor is an opaque material which is obtained by coating a suitable carrier with a powdered phosphor to thus give only a superficial emission.

As such a glass utilizing fluorescence of divalent Eu, there have hitherto been proposed the glasses described in Japanese Patent Publication No. 99609/1974 and a glass utilizing fluorescence of trivalent Eu has already been proposed by the inventors of the present Application (Japanese Patent Application No. 266759/1994).

In the glasses described therein, however, the phosphors exhibit weak emission and look violet or red, not blue.

Eu is ordinarily present in the trivalent state and exhibits red fluorescence by irradiation with ultraviolet rays. Thus, it is necessary to reduce Eu to the divalent state. Since divalent Eu exhibits fluorescences of various colors depending on the matrixes by irradiation with ultraviolet rays, the present invention aims at providing a fluorophosphate fluorescent glass exhibiting a strong blue fluorescence.

Up to the present time, no glass has been proposed which is caused to emit white color by mixing phosphors of the blue of divalent Eu, green of Tb and red of Mn or Sm in glass, since when a plurality of phosphors are contained in the glass, fluorescent intensity is reduced. Thus, the present invention aims are providing a fluorophosphate fluorescent glass exhibiting a strong white fluorescence by combination of the three primary colors in a glass containing blue of divalent Eu, green of Tb and Red of Mn or Sm.

It is an object of the present invention to provide a fluorophosphate fluorescent glass exhibiting a visible fluorescence, whereby the above described problems of the prior art can be overcome.

It is another object of the present invention to provide a fluorophosphate fluorescent glass exhibiting a strong blue fluorescence.

It is a further object of the present invention to provide a fluorophosphate fluorescent glass exhibiting a strong white fluorescence by combination of the three primary colors in a glass containing the blue of divalent Eu, green of Tb and red of Mn or Sm.

These objects can be attained by a fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, having a chemical composition comprising, at least, (I) phosphorus (P), oxygen (0) and fluorine (F), as glass constituting components, and (II) at least one member selected from divalent europium, terbium and (samarium + manganese), as a fluorescent agent, the divalent europium being contained as an essential component and at least one of samarium and manganese being contained as an essential component when terbium is present.

The accompanying drawings illustrate the principle and merits of the present invention.

Fig. 1 is a graph showing a fluorescent spectrum of divalent Eu ion when the glass prepared in Example 1 is excited by an ultraviolet ray of 365 nm.

Fig. 2 is a graph showing a fluorescent spectrum when the glass prepared in Example 24 is excited by an ultraviolet ray of 365 nm.

Fig. 3 is a graph showing a fluorescent spectrum when the glass prepared in Example 31 is excited by an ultraviolet ray of 365 nm.

Generally, according to the present invention, there is obtained a fluorophosphate fluorescent glass exhibiting a visible fluorescence, in particular, a fluorescent material comprising a fluorophosphate fluorescent glass containing divalent Eu capable of exhibiting a strong blue fluorescence by irradiating with ultraviolet rays and a fluorescent material comprising a fluorophosphate fluorescent glass containing divalent Eu, Tb and Mn or Sm capable of exhibiting a strong white fluorescence by irradiating with ultraviolet rays.

That is, according to the present invention, there is provided (1) a fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, having a chemical composition comprising, at least, (I) phosphorus (P),

oxygen (0) and fluorine (F), as glass constituting components, and (II) at least one member selected from . divalent europium, terbium and (samarium + manganese), as a fluorescent agent, the divalent europium being contained as an essential component and at least one of samarium and manganese being contained as an essential component when terbium is present.

(2) The fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, as described in the above (1), wherein the glass constituting components are represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

P	1 to 15 %,
Al	1 to 18 %
Mg	0 to 12 %,
Ca	0 to 18 %
Sr	0.5 to 21 %,
Ba	0 to 28 %
Zn	0 to 3.5 %,
Eu	0.001 to 0.8 %,
Ln	0 to 6.5 % (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Dy, Tb and Tm)
Ce	0 to 0.2 %
R	0 to 10 % (R: at least one atom selected from Li, Na and K),
O	4 to 55 %
F	15 to 70 % and
Cl	0 to 12 %

and a blue fluorescence is presented.

(3) The fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, as described in the above (1), wherein the glass constituting components are represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

P	1 to 15 %,
Al	1 to 18 %
Mg	0 to 12 %,
Ca	0 to 18 %

Sr	1 to 21	%,
Ba	0 to 28	%
Zn	0 to 3.5	%,
Eu	0.01 to 0.8	%,
Tb	0.2 to 4	%
Sm	0 to 3	%
Mn	0 to 1	%
	(at least one of Sm and Mn being present)	
Ln	0 to 4	% (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Dy and Tm)
Ce	0 to 0.2	%
R	0 to 3	% (R: at least one atom selected from Li, Na and K),
O	4 to 55	%
F	15 to 70	% and
Cl	0 to 10	%

and a white fluorescence is presented.

The reasons for limiting the composition range of each component of this fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, as described above are as follows:

P is a glass-forming component, which is generally present in a proportion of 1 to 15 %, since if less than the lower limit, glass formation is difficult, while if more than the upper limit, the durability is degraded. The preferred range is 1 to 13 % in the case of the above described glass (2), and 1 to 12 % in the case of the above described glass (3).

Al is a component for increasing the viscosity of the glass and suppressing crystallization, which is generally present in a proportion of 1 to 18 %, since if more than the upper limit, the melting property is lowered and the glass is unstable. The-preferred range is 2 to 12 % in the case of the above described glass (2), and 3 to 10 % in the case of the above described glass (3).

Mg, Ca, Sr, Ba and Zn are components for improving the melting property of the glass. If more than the above described ranges, the glass is unstable and tends to be crystallized. The preferred ranges are respectively 0 to 12 % of Mg, 0 to 18 % of Ca, 0.5 to 21 % of Sr, 0 to 28 % of Ba and 0 to 3.5 % of Zn. The more preferred ranges are respectively 0 to 6 % of Mg, 0 to 11 % of Ca, 1.5 to 12 % of Sr, 0 to 17 % of Ba and 0 to 2 % of Zn in the case of the above described glass (2) and the more preferred ranges are respectively 0 to 6 % of Mg, 0 to 11 % of Ca, 1.5 to 12 % of Sr, 0 to 17 % of Ba and 0 to 2 % of Zn in the case of the above described glass (3).

R (at least one atom selected from Li, Na and K) acts to lower the melting temperature of a glass melt, which is generally present in a proportion of 0 to 10 %, since if exceeding the above described range, the water resisting property is reduced and the devitrification tendency is increased, thus rendering the glass unstable. The preferred range is 0 to 3 %.

Eu is an important component capable of presenting fluorescence in the visible region by ultraviolet excitation, in particular, capable of presenting a blue fluorescence by reduction. This component should be present in a proportion of 0.001 to 0.8 %, since if less than the lower limit, sufficient fluorescence cannot be obtained, while if more than the upper limit, the fluorescence is reduced due to concentration quenching. The preferred range of Eu is 0.001 to 0.2 % in the case of the above described glass (2) and 0.01 to 0.4 % in the case of the above described glass (3).

Tb is an important component capable of presenting a green fluorescence in the visible region by ultraviolet exci-

tation. If more than the above described range, a glass is hardly obtained. The preferred range is 0.2 to 3.5 %.

Sm is an important component capable of presenting a red fluorescence in the visible region by ultraviolet excitation. If more than the above described range, the glass is strongly colored. The preferred range is 0 to 2.7 %.

Mn is an important component capable of presenting a red fluorescence in the visible region by ultraviolet excitation. If more than the above described range, the fluorescence is weakened. The preferred range is 0 to 0.6 %.

In the above described glass (2), Ln (at least one atom selected from Y, La, Gd, Yb, Lu, Dy, Tb and Tm) is a component for increasing the viscosity of the glass and suppressing crystallization. If more than the above described range, the effect thereof is weakened. The preferred range is 0 to 4 %.

In the above described glass (3), Ln (at least one atom selected from Y, La, Gd, Yb, Lu, Dy and Tm) is a component for increasing the viscosity of the glass and suppressing crystallization. If more than the above described range, the effect thereof is weakened. The preferred range is 0 to 3 %.

Ce is a component acting as a sensitizer of the fluorescent agent, but if exceeding the above described upper limit, this effect is decreased.

F and O are glass-forming components. If the amounts thereof are less than or more than the above described ranges, a glass is hardly obtained. The preferred range of F is 15 to 70 % in the above described glass (2) and 25 to 65 % in the above described glass (3). The preferred range of O is 4 to 55 % in the above described glass (2) and 6 to 40 % in the above described glass (3).

Cl is a component for intensifying the emission of divalent Eu. The emission thereof is intensified with increase of the divalent Eu, but the glass is unstable. The preferred range of Cl is 0 to 12 % in the case of the above described glass (2) and 0 to 6 % in the case of the above described glass (3).

Production of the fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, i.e. blue fluorescence or white fluorescence according to the present invention is carried out by mixing the corresponding raw material compounds to the proportion of the object composition, for example, aluminum phosphate, strontium fluoride, barium fluoride, europium oxide and terbium oxide, melting the resulting mixture at a temperature of 900 to 1300 °C for 1 to 2 hours in a reducing atmosphere, for example, hydrogen or carbon monoxide or in the presence of a metallic powder, for example, aluminum, zinc, calcium or magnesium, as a reducing agent inert to the glass composition and allowing the mixture to flow out into a metallic mold, followed by shaping.

The features and preferred embodiments of the present invention are described below:

(1) A fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, having a chemical composition comprising, at least, (I) phosphorus (P), oxygen (0) and fluorine (F), as glass constituting components, and (II) at least one member selected from divalent europium, terbium and (samarium + manganese), as a fluorescent agent, the divalent europium being contained as an essential component and at least one of samarium and manganese being contained as an essential component when terbium is present.

(2) A fluorophosphate fluorescent glass capable of exhibiting a blue fluorescence in the visible region, as described above in item (1), having the following chemical composition shown in Table 1 and represented in terms of atoms for making up the glass (mol %):

Table 1

P	1 ~ 13
Al	2 ~ 12
Mg	0 ~ 6
Ca	0 ~ 11
Sr	1.5 ~ 12
Ba	0 ~ 17
Zn	0 ~ 2
R	0 ~ 3.2
Eu	0.001 ~ 0.2
Ln	0 ~ 4
Ce	0 ~ 0.2
O	4 ~ 55
F	15 ~ 70
Cl	0 ~ 12

wherein R is at least one atom selected from Li, Na and K, Ln is and Ln is at least one atom selected from Y, La, Gd, Yb, Lu, Dy, Tb and Tm.

(3) A fluorophosphate fluorescent glass capable of exhibiting a blue fluorescence in the visible region, as described above in item (1), having the following chemical composition shown in Table 2 and represented in terms of atoms for making up the glass (mol %):

Table 2

P	1.4 ~ 4.9
Al	8.4 ~ 11.6
Mg	0 ~ 3.6
Ca	0 ~ 11
Sr	4.3 ~ 6.35
Ba	0 ~ 7.2
Eu	0.001 ~ 0.2①
Y	0 ~ 3.3①
La	0 ~ 3.3①
Gd	0 ~ 3.3①
Yb	0 ~ 3.3①
Lu	0 ~ 3.3①
Dy	0 ~ 3.3①
Tb	0 ~ 3.3①
Tm	0 ~ 3.3①

Table 2 (continued)

Ce	0 ~ 0.2
O	4.3 ~ 17.5
F	47 ~ 66
Cl	0 ~ 12

wherein the sum of ① = 0.001 ~ 3.3 %.

(4) A fluorophosphate fluorescent glass capable of exhibiting a white fluorescence in the visible region, as described above in item (1), having the following chemical composition shown in Table 3 and represented in terms of atoms for making up the glass (mol %):

Table 3

P	1 ~ 12
Al	3 ~ 10
Mg	0 ~ 6
Ca	0 ~ 11
Sr	1.5 ~ 12
Ba	0 ~ 17
Zn	0 ~ 2
R	0 ~ 3
Mn	0 ~ 0.6 ①
Sm	0 ~ 2.7 ①
Tb	0.2 ~ 3.5
Eu	0.01 ~ 0.4
Ln	0 ~ 3
Ce	0 ~ 0.2
O	6 ~ 40
F	25 ~ 65
Cl	0 ~ 6

wherein R is at least one atom selected from Li, Na and K, Ln is at least one atom selected from Y, La, Gd, Yb, Lu, Dy, Tb and Tm, and either of Sm or Mn of ① or both of them are present.

(5) A fluorophosphate fluorescent glass capable of exhibiting a white fluorescence in the visible region, as described above in item (1), having the following chemical composition shown in Table 4 and represented in terms of atoms for makingup the glass (mol %):

Table 4

P	1 ~ 11
Al	3 ~ 10
Mg	0 ~ 3
Ca	0 ~ 11
Sr	1.5 ~ 7
Ba	0 ~ 9
Zn	0 ~ 1
R	0 ~ 1
Mn	0 ~ 0.6 ①
Sm	0 ~ 2.7 ①
Tb	0.2 ~ 3.5
Eu	0.01 ~ 0.4
Ln	0 ~ 3
Ce	0 ~ 0.2
O	6 ~ 40

Table 4 (continued)

F	25 ~ 65
Cl	0 ~ 6

wherein R is at least one atom selected from Li, Na and K, Ln is at least one atom selected from Y, La, Gd, Yb, Lu, Dy, Tb and Tm, and either of Sm or Mn of ① or both of them are present.

Examples

The present invention will now be illustrated in greater detail by the following examples, but the present invention and the merits thereof are not intended to be limited by the materials, compositions and production procedures described in these examples.

Example 1

Using compounds shown in Table 5 as raw materials, the raw materials were mixed in a proportion by weight as in Sample No. 1, melted at 900 to 1300 °C, allowed to flow into a graphite mold and shaped to obtain a glass in stable manner.

The thus prepared glass was excited by an ultraviolet ray of 365 nm to obtain a fluorescent spectrum as shown in Fig. 1. The emission at 410 nm in Fig. 1 was due to divalent Eu ion, which was observed as blue with the naked eye.

Examples 2 to 23

Glasses were stably obtained by preparing raw materials in proportions by weight shown in Table 5, Sample Nos. 2 to 23 (by mol % of atoms shown in Table 6) and melting the mixture in the manner similar to Example 1.

When the glasses obtained in Examples 2 to 23 were also excited by an ultraviolet ray of 365 nm, there were obtained spectra similar to Example 1, presenting a blue fluorescence.

Table 5 (g)

Raw Material	Sample No. 1	2	3	4	5	6	7
$Al(PO_3)_3$	2.7	3.0	3.0	3.0	2.6	2.6	5.0
$Ba(PO_3)_2$	2.7	3.0	3.0	3.0	2.6	2.6	5.0
AlF_3	24.7	26.9	26.8	26.8	23	23.3	31.7
MgF_2	3.7	7.7	7.7	7.7	3.4	3.5	5.5
CaF_2	17.7	19.2	19.1	19.1	11.8	13.3	17.5
SrF_2	25.5	27.6	27.6	27.6	20.5	21.9	21.6
BaF_2					14.9	7.6	11.9
$BaCl_2$	22.8	12.3	12.3	12.3	21.2	25.1	
Al	0.01	0.01	0.01	0.01	0.01	0.01	
Zn							0.08
Eu_2O_3	0.2	0.2	0.2	0.2	0.1	0.2	0.3
Y_2O_3							
La_2O_3							
Gd_2O_3							
Yb_2O_3				0.4			
Dy_2O_3							
Tm_2O_3							
Tb_2O_3			0.2				
CeO_2		0.1	0.1				
LiF							
NaF							1.0
KF							

Table 5 (continued) (g)

Raw Material	Sample No. 8	9	10	11	12	13	14
$Al(PO_3)_3$	12.0	11.8	25.6	11.8	11.7	12	12
$Ba(PO_3)_2$	1.0	1.0		1.0	1.0	1.0	1.0
AlF_3	18.1	17.8		17.8	17.5	18.0	18.0
MgF_2	3.8	3.8		3.7	3.6	3.7	3.7
CaF_2	10.0	9.9		6.9	6.8	7.0	7.0
SrF_2	20.0	19.8	20.3	19.7	19.5	20.0	19.9
BaF_2	25.0	17.9	43.3	21.0	14.2	27.9	27.9
$BaCl_2$		8.1		7.9	15.5		
Al	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Zn							
Eu_2O_3	0.3	0.3	0.2	0.3	0.3	0.3	0.3
Y_2O_3							
La_2O_3			10.5				
Gd_2O_3	9.5	9.4		9.8	9.7	8.3	8.3
Yb_2O_3							
Dy_2O_3							1.7
Tm_2O_3						1.8	
Tb_2O_3							
CeO_2							
LiF							
NaF	0.2	0.2		0.2	0.2	0.2	0.2
KF							

Table 5 (continued) (g)

Raw Material	Sample No. 15	16	17	18	19	20	21	22	23
$Al(PO_3)_3$	28.9	28.6	28.4	28.3	28.0	26.3	12.4	28.2	8.4
$Ba(PO_3)_2$							1.0		
AlF_3							18.7		28.4
MgF_2				3.7			3.9		3.3
CaF_2					4.6		7.3		33.0
SrF_2	22.9	22.7	22.5	22.5	22.2	20.9	20.7	22.3	26.6
BaF_2	42.7	42.3	41.9	41.8	41.4	38.8	29.0	41.6	
$BaCl_2$						12.9			
Al							0.01		
Zn	0.1	0.1	0.1	0.1	0.1	0.1		0.2	
Eu_2O_3	1.1	1.1	1.1	1.0	1.0	1.0	0.3	2.1	0.4
Y_2O_3							6.4		
La_2O_3									
Gd_2O_3	2.6	2.6	2.6	2.6	2.6				
Yb_2O_3									
Dy_2O_3									
Tm_2O_3								2.3	
Tb_2O_3									
CeO_2									
LiF	1.6								
NaF		2.5					0.2		
KF			3.5					3.3	

Table 6 (mol%)

Glass Composition (atom)	Sample No. 1	2	3	4	5	6	7
P	1.6	1.6	1.6	1.6	1.6	1.6	2.5
Al	9.6	9.6	9.6	9.6	9.6	9.6	10.9
Mg	1.8	3.6	3.6	3.6	1.8	1.8	2.4
Ca	7.1	7.1	7.1	7.1	5.1	5.7	6.2
Sr	6.4	6.4	6.4	6.3	5.5	5.8	4.7
Ba	3.7	2.0	2.0	2.0	6.6	5.7	2.4
Zn							0.01
Li							
Na							0.7
K							
Eu	0.01	0.01	0.01	0.01	0.01	0.01	0.03
Y							
La							
Gd							
Yb				0.06			
Dy							
Tm							
Tb			0.03				
Ce		0.01	0.01				
O	4.7	4.8	4.8	4.8	4.7	4.7	7.6
F	58.3	61.7	61.6	61.6	58.3	57.1	62.5
Cl	6.9	3.4	3.4	3.4	6.9	8.0	

Table 6 (continued) (mol%)

Glass Composition (atom)	Sample No. 8	9	10	11	12	13	14
P	4.6	4.6	11.0	4.7	4.7	4.7	4.7
Al	8.4	8.6	3.7	8.6	8.6	8.6	8.6
Mg	2.0	2.0		2.0	2.0	2.0	2.0
Ca	4.1	4.1		3.0	3.0	3.0	3.0
Sr	5.1	5.1	6.1	5.2	5.2	5.2	5.2
Ba	4.7	4.7	9.3	5.4	5.4	5.4	5.4
Zn							
Li							
Na	0.2	0.2		0.2	0.2	0.2	0.2
K							
Eu	0.03	0.03	0.02	0.03	0.03	0.03	0.03
Y							
La			2.4				
Gd	1.7	1.7		1.8	1.8	1.5	1.5
Yb							
Dy							0.3
Tm						0.3	
Tb							
Ce							
O	16.5	16.5	36.6	16.9	16.9	16.9	16.9
F	52.6	50.0	30.8	49.7	47.2	52.2	52.2
Cl		2.5		2.5	5.0		

Table 6 (continued) (mol%)

Glass Composition (atom)	Sample No. 15	16	17	18	19	20	21	22	23
P	11.4	11.4	11.4	11.2	11.2	11.3	4.7	11.4	2.5
Al	3.8	3.8	3.8	3.7	3.7	3.8	8.6	3.8	9.7
Mg				2.1			2.0		1.4
Ca					2.1		3.0		11
Sr	6.4	6.4	6.4	6.2	6.2	6.3	5.2	6.3	5.5
Ba	8.5	8.5	8.5	8.3	8.3	10.7	5.4	8.5	
Zn	0.06	0.06	0.06	0.06	0.06	0.06		0.1	
Li	2.1								
Na		2.1					0.2		
K			2.1					2.1	
Eu	0.1	0.1	0.1	0.1	0.1	0.1	0.03	0.2	0.6
Y							1.8		
La									
Gd	0.5	0.5	0.5	0.5	0.5				
Yb									
Dy									
Tm								0.42	
Tb									
Ce									
O	35.4	35.4	35.4	34.6	34.6	34.1	16.9	35.5	7.5
F	31.8	31.8	31.8	33.2	33.2	29.2	52.2	31.7	62.3
Cl						4.7			

Comparative Example

Raw materials were mixed in a proportion by weight, calculated from a glass composition of the prior art, i.e. 75 % of B_2O_3, 12 % of Na_2O, 4 % of SrO, 4 % of Al_2O_3, 1 % of La_2O_3, 0.125 % of Eu_2O_3 and 0.1 % of C, melted at 1100 °C, allowed to flow out into a graphite mold and shaped to obtain a glass.

When the thus prepared glass was excited by an ultraviolet ray of 365 nm and subjected to measurement of its

fluorescence spectrum, there was obtained a similar spectrum to Example 1, presenting a light violet fluorescence. However, the emission intensity was 1/10 times as large as that of Example 1, even taking the highest peak at 410 nm.

Example 24

Using compounds shown in Table 7 as raw materials so as to give a composition shown in Table 8, the raw materials were mixed in a proportion by weight as in Sample No. 24, melted at 900 to 1300°C for 1 to 2 hours in a reducing atmosphere, for example, hydrogen or carbon monoxide, or in the presence of a metallic powder, for example, aluminum or zinc as a reducing agent inert to the glass compositions in nitrogen atmosphere, allowed to flow into a graphite mold and shaped to obtain a glass in stable manner.

When the thus prepared glass was excited by an ultraviolet ray of 365 nm, a white fluorescence was exhibited to give a fluorescent spectrum as shown in Fig. 2.

Examples 25 to 30

Glasses were stably obtained by preparing raw materials in proportions by weight shown in Table 7, Sample Nos. 25 to 30 and melting the mixture in the manner similar to Example 24.

When the glasses obtained in Examples 25 to 30 were also excited by an ultraviolet ray of 365 nm, there were obtained spectra similar to Example 24, presenting a white fluorescence.

Example 31

Using compounds shown in Table 7 as raw materials so as to give the composition shown in Table 8, the raw materials were mixed in a proportion by weight as in Sample No. 31, melted at 900 to 1300°C for 1 to 2 hours in a reducing atmosphere, for example, hydrogen or carbon monoxide, or in the presence of a metallic powder, for example, aluminum or zinc as a reducing agent inert to the glass compositions in nitrogen atmosphere, allowed to flow into a graphite mold and shaped to obtain a glass in stable manner.

When the thus prepared glass was excited by an ultraviolet ray of 365 nm, a white fluorescence was exhibited to give a fluorescent spectrum as shown in Fig. 3.

Examples 32 to 38

Glasses were stably obtained by preparing raw materials in proportions by weight shown in Table 7, Sample Nos. 32 to 38 and melting the mixture in the manner similar to Example 31.

When the glasses obtained in Examples 32 to 38 were also excited by an ultraviolet ray of 365 nm, there were obtained spectra similar to Example 31, presenting a white fluorescence.

Table 7 (g)

Raw Material	Sample No. 24	25	26	27	28	29	30
$Al(PO_3)_3$	7.5	24.9	25.0	25.2	8.2	6.1	13.4
AlF_3	23.3				27.8	26.1	17.9
MgF_2	3.6				3.2	3.6	3.3
CaF_2	19.0				31.5	22.0	7.1
SrF_2	25.0	20.0	20.1	20.2	26.0	26.8	20.1
BaF_2		40.0	40.3	39.9		13.6	28.0
$BaCl_2$	15.0						
MnO_2							
Sm_2O_3	0.4	0.2	12.5	0.4	0.7	0.3	1.3
Tb_2O_3	6.0	14.7	1.9	1.0	2.3	1.1	8.3
Eu_2O_3	0.2	0.2	0.2	1.9	0.4	0.3	0.3
Gd_2O_3				10.9			
CeO_2				0.5			
Zn							
Al		0.01	0.01	0.10	0.03	0.03	0.02
KF							0.2

Table 7 (continued) (g)

Raw Material	Sample No. 31	32	33	34	35	36	37	38
$Al(PO_3)_3$	7.1	9.4	9.4	9.4	25.4	26.8	7.4	8.0
AlF_3	23.3	23.9	23.9	23.9			24.3	27.1
MgF_2	3.6	2.8	2.8	2.8			3.8	6.3
CaF_2	18.9	19.8	19.7	19.7			19.7	30.0
SrF_2	24.8	22.3	22.3	22.3	20.4	21.5	25.8	6.3
BaF_2					40.2	42.5	11.0	17.7
$BaCl_2$	14.9	14.8	14.8	14.8				
MnO_2	0.1	0.1	0.2	0.2	0.5	1.5	0.8	0.4
Sm_2O_3								
Tb_2O_3	6.9	6.5	6.5	6.5	13.3	7.2	6.8	3.7
Eu_2O_3	0.3	0.3	0.3	0.3	0.2	0.2	0.3	0.4
Gd_2O_3								
CeO_2								
Zn	0.1	0.1	0.2					
Al				0.07	0.10	0.30	0.18	0.14
KF								

Table 8 (mol%)

Glass Composition (atom)	Sample No. 24	25	26	27	28	29	30
P	2.6	10.9	10.9	10.9	2.5	2.0	5.0
Al	9.3	3.7	3.7	3.8	9.7	9.7	8.7
Mg	1.8				1.4	1.7	1.7
Ca	7.4				10.7	8.1	3.0
Sr	6.1	6.1	6.1	6.2	5.5	6.2	5.2
Ba	2.2	8.8	8.8	8.7		2.2	5.2
Zn							
Na							0.1
Mn							
Sm	0.07	0.04	2.74	0.08	0.11	0.06	0.25
Tb	1.0	3.1	0.4	0.2	0.3	0.2	1.5
Eu	0.03	0.04	0.04	0.41	0.06	0.06	0.05
Gd				2.3			
Ce				0.1			
O	9.4	37.5	37.5	37.5	8.2	6.5	17.7
F	55.8	29.9	29.9	29.8	61.6	63.3	51.5
Cl	4.4						

Table 8 (continued) (mol%)

Glass Composition (atom)	Sample No. 31	32	33	34	35	36	37	38
P	2.5	3.2	3.2	3.2	11.0	11.2	2.5	2.5
Al	9.3	9.6	9.6	9.7	3.8	4.1	9.5	9.8
Mg	1.8	1.3	1.3	1.3			1.8	2.8
Ca	7.4	7.6	7.6	7.6			7.4	10.5
Sr	6.0	5.3	5.3	5.3	6.2	6.3	6.0	1.4
Ba	2.2	2.1	2.1	2.1	8.7	8.9	1.8	2.8
Zn	0.1	0.1	0.1					
Na								
Mn	0.03	0.03	0.05	0.05	0.20	0.62	0.27	0.11
Sm								
Tb	1.2	1.1	1.1	1.1	2.8	1.4	1.1	0.6
Eu	0.05	0.05	0.05	0.05	0.04	0.04	0.05	0.06
Gd								
Ce								
O	9.3	11.3	11.4	11.4	37.5	37.0	9.7	8.6
F	55.9	54.1	54.0	54.0	29.8	30.4	59.8	61.1
Cl	4.4	4.3	4.3	4.3				

The fluorescent glass of the present invention is capable of converting invisible ultraviolet rays into visually observable visible rays with high efficiency and is available for controlling the optical axis of a laser beam such as an excimer laser. Furthermore, according to the present invention, there can be provided a fluorophosphate fluorescent glass exhibiting a strong blue fluorescence, which is applicable to fluorescent displaying of full color in combination with a green or red fluorescent glass or a fluorophosphate fluorescent glass exhibiting white fluorescence, which can be utilized for display devices and backlights of LCDs.

Claims

1. A fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, having a chemical composition comprising, at least, (I) phosphorus (P), oxygen (0) and fluorine (F), as glass constituting components, and (II) at least one member selected from divalent europium, terbium and (samarium + manganese), as a fluorescent agent, the divalent europium being contained as an essential component and at least one of samarium and manganese being contained as an essential component when terbium is present.

2. A fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, as claimed in Claim 1, wherein the glass constituting components are represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

P	1 to 15 %,
Al	1 to 18 %
Mg	0 to 12 %,
Ca	0 to 18 %
Sr	0.5 to 21 %,
Ba	0 to 28 %
Zn	0 to 3.5 %,
Eu	0.001 to 0.8 %,
Ln	0 to 6.5 % (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Dy, Tb and Tm)
Ce	0 to 0.2 %
R	0 to 10 % (R: at least one atom selected from Li, Na and K),
O	4 to 55 %
F	15 to 70 % and
Cl	0 to 12 %

and a blue fluorescence is presented.

3. A fluorophosphate fluorescent glass capable of exhibiting fluorescence in the visible region, as claimed in Claim 1, wherein the glass constituting components are represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

P	1 to 15 %,
Al	1 to 18 %
Mg	0 to 12 %,
Ca	0 to 18 %
Sr	1 to 21 %,
Ba	0 to 28 %
Zn	0 to 3.5 %,
Eu	0.01 to 0.8 %,
Tb	0.2 to 4 %
Sm	0 to 3 %
Mn	0 to 1 %
	(at least one of Sm and Mn being contained)
Ln	0 to 4 % (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Dy, and Tm)
Ce	0 to 0.2 %
R	0 to 3 % (R: at least one atom selected from Li, Na and K),
O	4 to 55 %
F	15 to 70 % and
Cl	0 to 10 %

and a white fluorescence is presented.

4. A fluorophosphate fluorescent glass capable of exhibiting a blue fluorescence in the visible region, as claimed in claim 2, wherein the glass constituting components are represented, in terms of atoms for making up the glass, by the following chemical composition (mol %):

P	1 to 13 %
Al	2 to 12 %
Mg	0 to 6 %

Ca	0 to 11 %
Sr	1.5 to 12 %
Ba	0 to 17 %
Zn	0 to 2 %
R	0 to 3.2%
Eu	0.001 to 0.2%
Ln	0 to 4 %
Ce	0 to 0.2%
O	4 to 55 %
F	15 to 70 % and
Cl	0 to 12 %

wherein R is at least one atom selected from Li, Na and K, Ln is and Ln is at least one atom selected from Y, La, Gd, Yb, Lu, Dy, Tb and Tm.

5. A fluorophosphate fluorescent glass capable of exhibiting a blue fluorescence in the visible region, as claimed in Claim 2, wherein the glass constituting components are represented, in terms of atoms for making up the glass, by the following chemical composition (mol %):

P	1.4 to 4.9
Al	8.4 to 11.6
Mg	0 to 3.6
Ca	0 to 11
Sr	4.3 to 6.35
Ba	0 to 7.2
Eu	0.001 to 0.2 ①
Y	0 to 3.3 ①
La	0 to 3.3 ①
Gd	0 to 3.3 ①
Yb	0 to 3.3 ①
Lu	0 to 3.3 ①
Dy	0 to 3.3 ①
Tb	0 to 3.3 ①
Tm	0 to 3.3 ①
Ce	0 to 0.2
O	4.3 to 17.5
F	47 to 66 and
Cl	0 to 12

wherein the sum of ① = 0.001 ~ 3.3 %.

6. A fluorophosphate fluorescent glass capable of exhibiting a white fluorescence in the visible region, as claimed in Claim 3, wherein the glass constituting components are represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

P	1 to 12
Al	3 to 10
Mg	0 to 6
Ca	0 to 11
Sr	1.5 to 12
Ba	0 to 17
Zn	0 to 2

(continued)

R	0 to 3
Mn	0 to 0.6①
Sm	0 to 2.7①
Tb	0.2 to 3.5
Eu	0.01 to 0.4
Ln	0 to 3
Ce	0 to 0.2
O	6 to 40
F	25 to 65 and
Cl	0 to 6

wherein R is at least one atom selected from Li, Na and K, Ln is at least one atom selected from Y, La, Gd, Yb, Lu, Dy and Tm, and either of Sm or Mn of①or both of them are present.

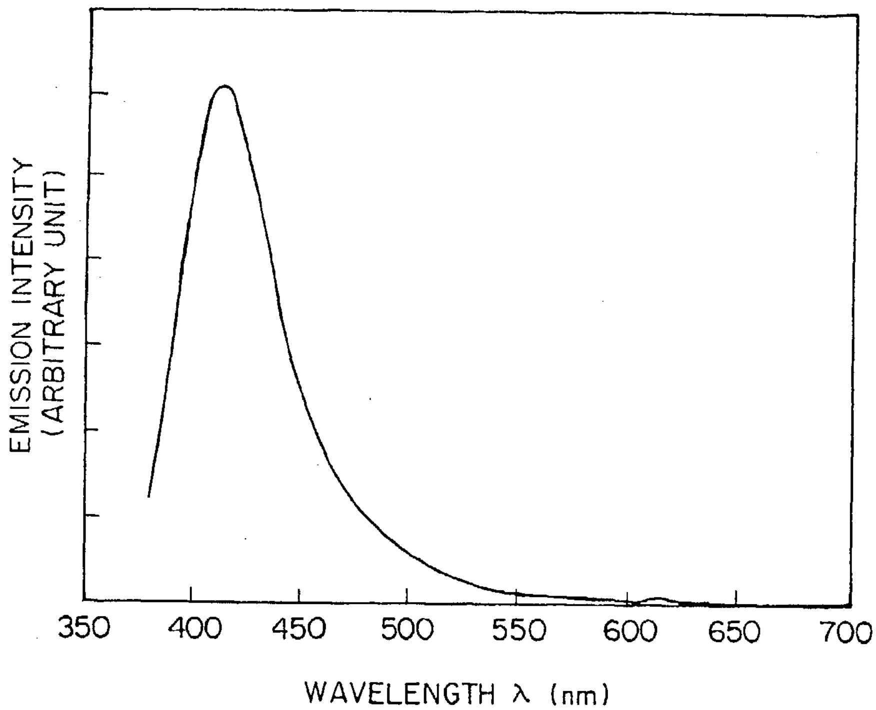
7. A fluorophosphate fluorescent glass capable of exhibiting a white fluorescence in the visible region, as claimed in Claim 3, wherein the glass constituting components are represented, in term of atoms for making up the glass, by the following chemical compsition (mol %):

P	1 to 11
Al	3 to 10
Mg	0 to 3
Ca	0 to 11
Sr	1.5 to 7
Ba	0 to 9
Zn	0 to 1
R	0 to 1
Mn	0 to 0.6①
Sm	0 to 2.7①
Tb	0.2 to 3.5
Eu	0.01 to 0.4
Ln	0 to 3
Ce	0 to 0.2
O	6 to 40
F	25 to 65 and
Cl	0 to 6

wherein R is at least one atom selected from Li, Na and K, Ln is at least one atom selected from Y, La, Gd, Yb, Lu, Dy and Tm, and either of Sm or Mn of①or both of them are present.

8. A display device or backlight of an LCD whenever comprising a fluorophosphate fluorescent glass as claimed in any one of the preceding claims.

FIG. 1


EMISSION INTENSITY
(ARBITRARY UNIT)
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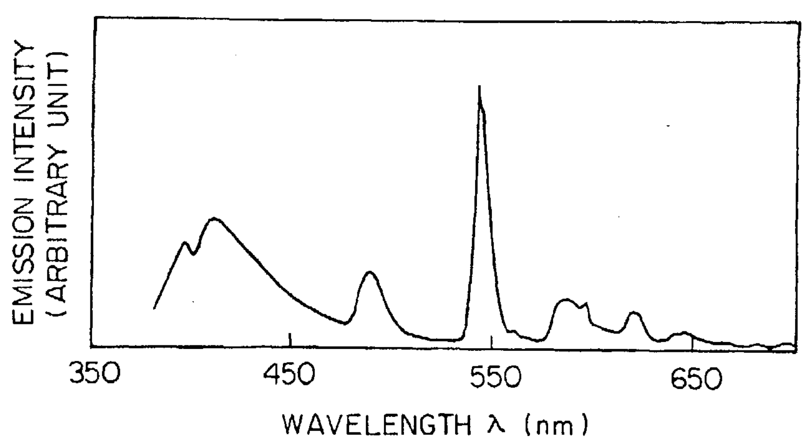
400
450
500
550
600
650
700
WAVELENGTH λ (nm)

FIG. 2


EMISSION INTENSITY
(ARBITRARY UNIT)
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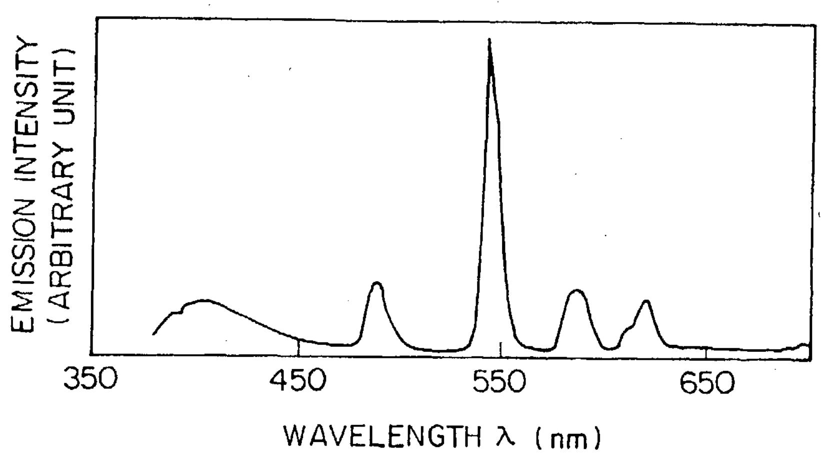
550
650
WAVELENGTH λ (nm)

FIG. 3


EMISSION INTENSITY
(ARBITRARY UNIT)
350
450
550
650
WAVELENGTH λ (nm)

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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 8394

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	PHYSICAL REVIEW B (CONDENSED MATTER), 1 APRIL 1996, APS THROUGH AIP, USA, vol. 53, no. 14, ISSN 0163-1829, pages R8821-R8823, XP002025046 BRUNDAGE R T ET AL: "Homogeneous linewidth of the /sup 5/D/sub 0/-/sup 7/F/sub 0/ transition of trivalent europium in a fluorophosphate glass" * page R8821, right-hand column, paragraph 2 - paragraph 5 * ---	1,2,4,5	C03C3/247 C03C4/12
A	FIZIKA I KHIMIYA STEKLA, JAN.-FEB. 1993, RUSSIA, vol. 19, no. 1, ISSN 0132-6651, pages 20-23, XP002025047 DMITRYUK A V ET AL: "Electron phototransfer spectroscopy in europium-doped phosphate glasses" * the whole document * ---	1-8	
D,A	DATABASE WPI Section Ch, Week 7514 Derwent Publications Ltd., London, GB; Class L01, AN 75-23099W XP002025049 & JP-A-49 099 609 (SANTOKU METAL INDUSTRY) , 20 September 1974 * abstract * ---	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C03C
A	EP-A-0 074 585 (TOKYO SHIBAURA ELECTRIC CO) 23 March 1983 * abstract * ---	1-8	
D,A, P	EP-A-0 709 345 (SUMITA OPTICAL GLASS) 1 May 1996 * claims * --- -/--	1-8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 February 1997	Van Bommel, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 96 30 8394

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	PHYSICAL REVIEW B (CONDENSED MATTER), 1 MARCH 1992, USA, vol. 45, no. 9, ISSN 0163-1829, pages 4620-4625, XP002025048 TANABE S ET AL: "Upconversion properties, multiphonon relaxation, and local environment of rare-earth ions in fluorophosphate glasses" * abstract * -----	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 February 1997	Van Bommel, L

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L : document cited for other reasons

& : member of the same patent family, corresponding document

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